<International Research Center for Elements Science>Organic Main Group Chemistry

International Research Center for Elements Science – Organic Main Group Chemistry –

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Prof Robin, B. Bedford University of Bristol, U.K., 21 November
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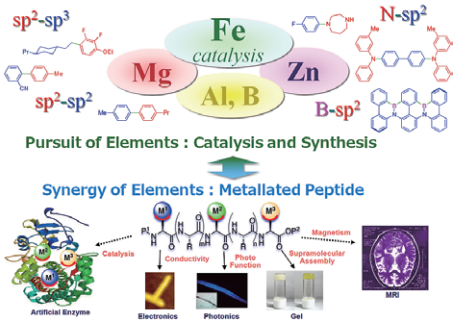
Scope of Research

Our research activity is focused on the development of molecular transformation reactions, which can provide new ways to exploit chemical resources, such as haloalkanes, alkenes, alcohol etc. The present research subjects are (1) metal-catalyzed C–C and C–N bond forming reactions by using universal metals such as iron, magnesium and aluminum (2) development of smart materials based on synergistic effect of various metals on artificial peptides (3) synthesis of heteroatom-fused π-conjugated molecules toward optoelectronics (4) understanding of synergistic effects of multi-element center interactions for the catalysis with the help of quantum chemical methods and synchrotron X-ray absorption spectroscopy.



KEYWORDS

Carbon–Carbon Bond Formation
Iron Catalyst
Cross-Coupling Reaction
Metallated Peptide
π-Conjugated Molecule

Selected Publications

Ghorai, S. K.; Jin, M.; Hatakeyama, T.; Nakamura, M., Cross-Coupling of Non-activated Chloroalkanes with Aryl Grignard Reagents in the Presence of Iron/*N*-Heterocyclic Carbene Catalysts, *Org. Lett.*, **14,** 1066-1069 (2012).

Hashimoto, T.; Hatakeyama, T.; Nakamura, M., Stereoselective Cross-Coupling between Alkenylboronates and Alkyl Halides Catalyzed by Iron-Bisphosphine Complexes, *J. Org. Chem.*, **77,** 1168-1173 (2012).

Isozaki, K.; Ogata, K.; Haga, Y.; Sasano, D.; Ogawa, T.; Kurata, H.; Nakamura, M.; Naota, T.; Takaya, H., Metal Array Fabrication through Self-assembly of Pt-complex-bound Amino Acids, *Chem. Commun.*, **48,** 3936-3988 (2012).

Hatakeyama, T.; Hashimoto, T.; Kathriarachchi, K. K. A. D. S.; Zenmyo, T.; Seike, H.; Nakamura, M., Iron-Catalyzed Alkyl-Alkyl Suzuki-Miyaura Coupling, *Angew. Chem. Int. Ed.*, **51,** 8834-8837 (2012).

Kawamura, S.; Kawabata, T.; Ishizuka, K.; Nakamura, M., Iron-Catalyzed Cross-Coupling of Halohydrins with Aryl Aluminium Reagents: a Protecting-group-free Strategy Attaining Remarkable Rate Enhancement and Diastereoinduction, *Chem. Commun.*, **48,** 9376-9378 (2012).

Hatakeyama, T.; Hashimoto, S.; Oba, T.; Nakamura, M., Azaboradibenzo[6]helicene: Carrier Inversion Induced by Helical Homochirality, *J. Am. Chem. Soc.*, **134,** 19600-19603 (2012).

Iron-Catalyzed Alkyl-Alkyl Suzuki-Miyaura Coupling

Suzuki-Miyaura coupling reaction is one of the most practical and reliable synthetic reactions for the production of functional molecules such as drug/agrochemical intermediates and organic electronic materials. We have developed an iron-catalyzed alkyl-alkyl Suzuki-Miyaura coupling of primary and secondary alkyl halides by using a $Fe(acac)_3$/Xantphos catalyst. The key to success is the use of *i*PrMgCl as an activator for trialkylboranes. The practicable functional-group compatibility and non-hazardous nature of the iron catalyst suggest that the present reaction is suitable for the facile synthesis of various functional molecules as illustrated by the synthesis of long-chain fatty acid derivatives.

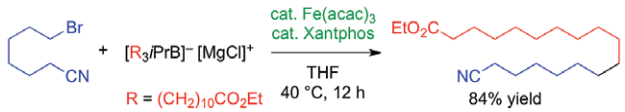


Figure 1. Iron-catalyzed alkyl-alkyl Suzuki-Miyaura coupling.

Metal Array Fabrication through Self-assembly of Pt-complex-bound Amino Acids

Supramolecular self-assembly of amino acids and peptides constitutes a rational approach to fabricating nanostructures comprising highly ordered arrays of functional groups with tailored chemical and physical properties. Indeed, this approach has been widely exploited using various artificial amino acids and peptides which conjugate to photoactive as well as electrically and catalytically active functional groups. Thus, a supramolecular architecture with a well-oriented and highly periodic array of functionalities can be obtained, even with enhanced inherent functions. However, metal array fabrication using such conjugates still remains a largely untouched field. We reported a Pt complex-bound glutamic acid as a building block for a supramolecular β-sheet structure that supports a highly oriented Pt array.

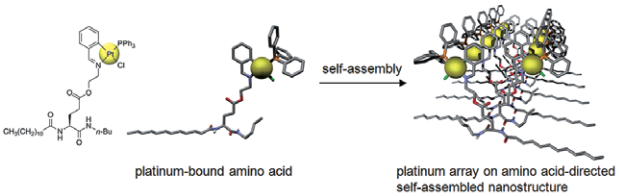


Figure 2. Metal array fabrication through self-assembly of Pt-complex-bound amino acids.

Carrier Inversion of Azaboradibenzo[6]-helicene Induced by Helical Homochirality

Recently, the self-assembly of helicenes via unique π-π stacking interactions in solution, as well as in crystals, has been studied extensively, since these aggregates display intriguing properties such as liquid crystallinity, nonlinear optical susceptibility, and circularly polarized luminescence. So far, however, the electrical properties of these aggregates have not been investigated well, even though the π-π stacking interactions are expected to facilitate charge transport. We have synthesized azaboradibenzo[6]-helicene via a tandem bora-Friedel–Crafts-type reaction and revealed that the racemate and single enantiomer are p-type and n-type semiconductors, respectively. This unprecedented carrier inversion can be explained by changes in the packing structure of the respective hetero and homochiral crystals, as revealed by electronic coupling calculations.

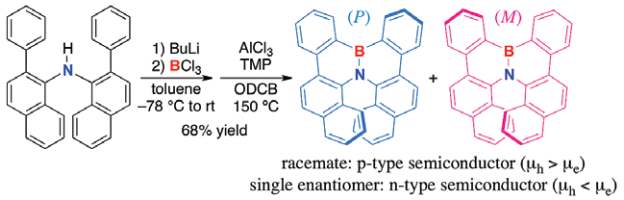


Figure 3. Synthesis and carrier inversion of azaboradibenzo[6]helicene.